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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FLUIDISING COMPOSITION

(57) Abstract: A fluidising admixture for use with sprayable cementitious compositions, the admixture consists of 2-phosphonobutane-1,2,4-tricarboxylic acid and at least one selected polymer derived from ethylenically-unsaturated mono- or dicarboxylic acids. Citric acid may optionally be present. The admixture has good fluidising properties and outstanding shelf-life.

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FLUIDISING COMPOSITION

This invention relates to the spraying of cementitious compositions and to admixtures for use in such spraying.

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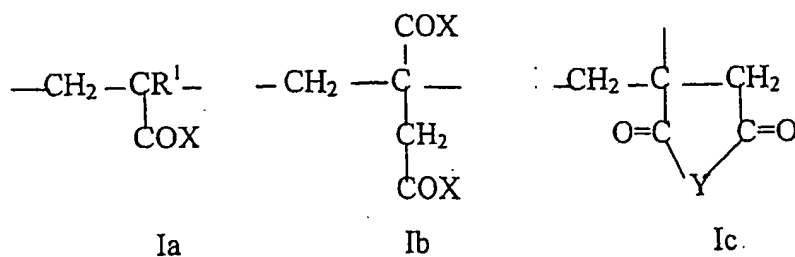
The spraying of cementitious compositions such as concrete is regularly used in a number of applications, most notably in tunnelling. It is a requirement that such compositions be able to be easily conveyed (usually by pumping) to a spray nozzle. This can be achieved by the addition to the cementitious composition that is to be pumped and sprayed, at the mix stage, of an admixture which confers improved fluidity of the mix. There is a considerable variety of such admixtures known to and used by the art.

It has now been found that an especially effective admixture may be prepared by the combination of particular selected components. The invention therefore provides a fluidising admixture for use with sprayable cementitious compositions, the admixture consisting of

- (1) 2-phosphonobutane-1,2,4-tricarboxylic acid;
- (2) optionally, citric acid; and
- (3) at least one polymer derived from ethylenically-unsaturated mono-or dicarboxylic acids, and characterised in that the polymer consists of
 - a) 51-95 mole % of moieties of formula 1a and/or 1b and/or 1c

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25



30

wherein R^1 = hydrogen or a C_{1-20} aliphatic hydrocarbon residue;
 $X = O_a M, -O-(C_m H_{2m} O)_n - R^2, -NH-(C_m H_{2m} O)_n - R^2,$

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M = hydrogen, a mono- or divalent metal cation, an ammonium ion or an organic amine residue;

a = 0.5 or 1;

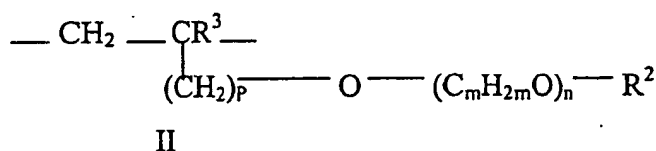
R² = hydrogen, C₁₋₂₀ aliphatic hydrocarbon, C₅₋₈ cycloaliphatic hydrocarbon or optionally substituted C₆₋₁₄ aryl residue;

Y = O, NR²;

m = 2-4; and

n = 0-200

b) 1-48.9 mole% of moieties of the general formula II

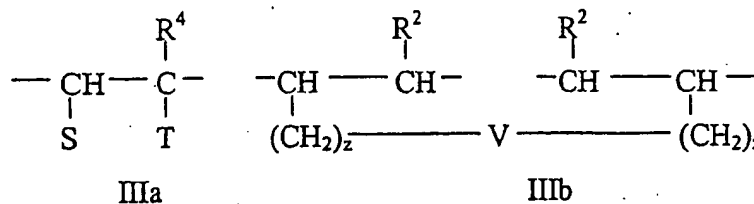


wherein R³ = hydrogen or C₁₋₅ aliphatic hydrocarbon;

p = 0-3; and

R² has the meaning given previously;

c) 0.1-5 mole % of moieties of Formulae IIIa or IIIb



wherein S = H, -COO_aM, -COOR⁵

T = U¹-(CH-CH₂-O)_x-(CH₂-CH₂O)_yR⁶

CH³

-W-R⁷

-CO-[NH-(CH₂)₃]_s-W-R⁷

-CO-O-(CH₂)₂-W-R⁷

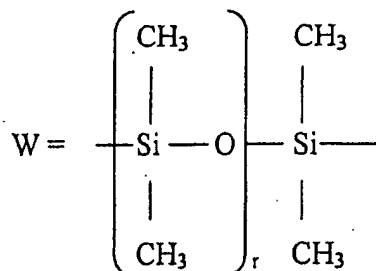
-(CH₂)₂-V-(CH₂)₂-CH=CH-R²

-COOR⁵ when S is -COOR⁵ or COO_aM

$U^1 = -CO-NH-, -O-, -CH_2O-$

$U^2 = -NH-CO-, -O-, -OCH_2-$

$V = -O-CO-C_6H_4-CO-O-$ or $-W-$



$R^4 = H, CH_3$

$R^5 = H, C_3-20$ aliphatic hydrocarbon residue, C_5-C_8

cycloaliphatic hydrocarbon residue or C_6-14 aryl residue;

$R^6 = R^2, -CH_2-\underset{\substack{| \\ R^4}}{CH}-U^2-\underset{\substack{| \\ R^4} \atop |}{C}=\underset{\substack{| \\ S}}{CH}$

$R^7 = R^2, -[(CH_2)_3-NH]_s-CO-\underset{\substack{| \\ R^4} \atop |}{C}=\underset{\substack{| \\ S}}{CH}$

$-(CH_2)_z-O-CO-\underset{\substack{| \\ R^4} \atop |}{C}=\underset{\substack{| \\ S}}{CH}$

wherein

$r = 2-100$

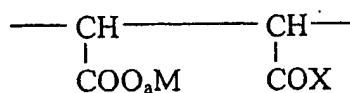
$s = 1, 2$

$x = 1-150$

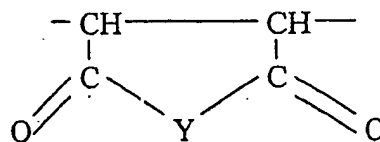
$y = 0-15$

$z = 0-4$

d) 0-47.9 mole % of moieties of the general formula IVa and / or IVb:



IVa



IVb

wherein a, M, X and Y have the significances hereinabove defined.

In a preferred embodiment of the invention, the polymer is characterised as follows - any moiety or group present in the polymer description hereinabove and not specifically mentioned in the following embodiment is absent from the embodiment, and any numerical value not specifically mentioned remains unaltered from that of the polymer description

5 hereinabove;

a) the moiety is according to formula Ia;

R^1, R^2 are independently H or CH_3 ;

$X = O_a M, -O-(C_m H_{2m} O)_n - R^2$

10 $M = H$ or a mono-or divalent metal cation;

$a = 1$;

$Y = O, NR^2$;

$m = 2-3$; and

$n = 20-150$;

15

b) R^2, R^3 are independently H or CH_3 ; and

$p = 0-1$;

c) the moiety is according to formula IIIa;

20 $S = H, -COO_a M, -COOR^5$

$T = U^1 - (CH-CH_2-O)_x - (CH_2-CH_2-O)_y R^6$
 $\quad \quad \quad |$
 $\quad \quad \quad CH^3$

$-CO-[NH-(CH_2)_3]_5-W-R^7$

$-CO-O-(CH_2)_z-W-R^7$

25 R^4, R^5 are independently H, CH_3 ;

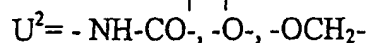
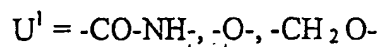
$R^6 = R^2, -CH_2-\underset{\substack{| \\ R^4}}{CH}-U^2-\underset{\substack{| \\ R^4}}{C}=\underset{\substack{| \\ S}}{CH}$

$R^7 = R^2, -[(CH_2)_3-NH]_5-CO-\underset{\substack{| \\ R^4}}{C}=\underset{\substack{| \\ S}}{CH}$

30

$-(CH_2)_z-O-CO-\underset{\substack{| \\ R^4}}{C}=\underset{\substack{| \\ S}}{CH}$

wherein



$$x = 20-50;$$

$$y = 1-10; \text{ and}$$

$$z = 0-2.$$

In a further preferred embodiment, the polymer is characterised as follows - any moiety or group present in the description of the preferred embodiment hereinabove and not specifically mentioned in the following further preferred embodiment is absent from the further preferred embodiment, and any numerical value not specifically mentioned remains unaltered from that of the preferred embodiment description hereinabove;

a) the moiety is according to formula Ia;

$$R^1 = \text{H};$$

$$R^2 = \text{CH}_3;$$

$$X = \text{O}_a \text{M};$$

M = a mono-or divalent metal cation;

$$Y = \text{O}, \text{NR}^2;$$

$$m = 2; \text{ and}$$

$$n = 25-50;$$

b) $R^2, R^3 = \text{H};$ and

$$p = 0;$$

c) the moiety is according to formula IIIa;

$$S = \text{H}, -\text{COO}_a\text{M};$$

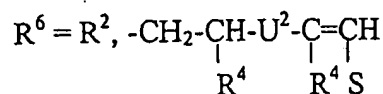
$$T = U^1 - (\text{CH}-\text{CH}_2-\text{O})_x - (\text{CH}_2-\text{CH}_2\text{O})_y R^6$$

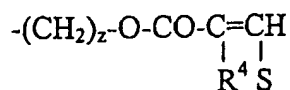
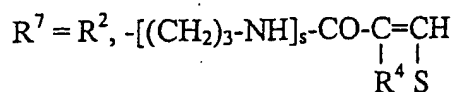
$$\quad \quad \quad |$$

$$\quad \quad \quad \text{CH}^3$$

$$-\text{CO}-\text{O}-(\text{CH}_2)_z-\text{W}-R^7$$

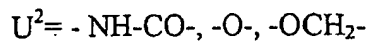
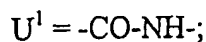
$$R^4, R^5 = \text{H};$$





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wherein



$$x = 20-50;$$

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$$y = 5-10; \text{ and}$$

$$z = 1-2.$$

The polymers for use in this invention preferably have a weight-average molecular weight of from 5000-50000, preferably from 10000-40000.

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Typical examples of preferred polymers may be prepared by the reaction of methoxypolyethyleneglycol-monovinyl ether, maleic anhydride, amine-terminated ethylene oxide-propylene oxide block copolymer and acrylic acid. Examples of these materials and their preparation may be found in International Application WO 00/77058 the contents of which are incorporated herein by reference.

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The invention also provides a method of imparting flow to a cementitious composition, comprising the addition thereto of an admixture as hereinabove described.

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The invention also provides a method of spraying a cementitious composition by preparing a cementitious mix and conveying the mix to a spray nozzle, there being added to the mix at preparation an admixture as hereinabove described.

The proportions of the solids of the three components in the admixture are as follows:

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	limits	more preferred	most preferred
Component 1	1-40	2-20	4-12
5 Component 2	0-40	2-20	4-12
Component 3	5-60	10-40	20-30

The admixture will always contain a proportion of water, and the admixture will never be
10 100% solids, as the "limits" and "more preferred" columns would seem to suggest is possible. However, the skilled person will be able to determine appropriate compositions in each case, by simple experimentation.

The admixture is added to a cementitious mixture at a rate of from 0.2-2.0%, preferably from
15 0.5 - 0.8% by weight solids on cement.

The admixture according to this invention may be used in conjunction with all the conventional admixtures used in the spraying of cementitious compositions, for example, the various accelerators commonly added at the spray nozzle. The admixture according to the
20 invention works well with both the classic alkali types (such as aluminates, caustic alkalis and "water glass") and the newer alkali-free, generally aluminium compound-based types.

The admixture according to the invention performs at least as well as known fluidity-improving admixtures. It has the additional major practical advantage of having a very long
25 shelf life. This means that it can be prepared well in advance of use and stored for several months without any segregation of ingredients. Moreover, it maintains this stability in the adverse conditions often found in tunnels, such as high temperatures, on exposure to which many conventional admixtures are no longer stable.

30 The invention is further described with reference to the following examples.

Example 1

Preparation and testing of an admixture according to the invention.

5 An admixture is prepared by mixing the following components

	polymer (44% aqueous solution) ¹	50 parts by weight
	water	36 parts
	2-phosphonobutane-1,2,4-tricarboxylic acid	
10	(50% aqueous solution)	7.8 parts
	citric acid monohydrate	7.1 parts

1. The material used is "MVA 2453 L/44%" ex Degussa.

15 This is added to a concrete mix of the following composition at a rate of 0.7 % solids on cement:

	Portland cement CEM I 42.5	450kg/m ³
	Aggregate 0-4mm	1165kg/m ³
20	4-8mm	500kg/m ³

having a water/cement ratio of 0.435.

As a comparison, there is added to samples of the same concrete mix the same proportion of
25 a high performance, commercially-available fluidising agent GLENIUM® T 803 ex MBT (Schweiz) AG. These mixes are tested by means of (a) a flow table, and (b) spraying.

The flow table tests are as follows:

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		Composition of invention	GLENIUM T 803
Water/ cement ratio		0.435	0.441
Flow table spread	[cm]		
1 h		52	54
2 h		50	52
3 h		47	49
4 h		45	47
Air content	[%]	3.0	2.6

For the spray testing, there is added at the nozzle in both cases 7% by weight on cement of a commercially-available shotcrete accelerator, MEYCO® SA160 (ex MBT (Schweiz) AG.

The compressive strength is measured in a variety of ways and over different times and the results are shown in the following table:

		Composition of invention	GLENIUM T 803
Compressive. Strength	[MPa]		
3 min. (penetronneedle) ²		0.12	0.06
6 min. (")		0.18	0.09
15 min. (")		0.19	0.20
30 min. (")		0.36	0.27
1 h (")		0.56	0.46
2 h (")		0.90	0.68
4 h (")		2.70 *	0.90
1 d (nail gun) ³		17.5	17.1
28 d (core) ⁴		41.7	45.8

2. A method for testing compressive strength, in which a metal needle is pushed into concrete and the resistance to its entry is measured. Suitable for relatively soft materials.
 3. A method for testing compressive strength, in which a metal nail is fired into a concrete and its penetration measured. Suitable for concretes at a later stage after setting.
 4. A method for testing compressive strength, in which a cylindrical core is drilled from a hardened concrete and tested on a testing apparatus.
- * This result had to be obtained by means of a nail gun, because the concrete is already too hard to use the penetronneedle method. On the other hand, the comparative example is too soft to allow use of the nail gun. This is an indication of the superior

early strength development of a concrete utilising the admixture of the present invention. Early strength development is very important in spraying concrete applications.

- 5 The admixture according to the invention has performance characteristics comparable with those of the high performance commercial material.

Example 2

- 10 Stability testing of the admixture of Example 1.

Samples of the admixture are tested in a mortar by flow table and for setting time. The mortar is a 1:3 blend of CEM I 42.5 Portland cement and CEM standard sand (according to DIN EN 196-1), and the admixture samples are added at a rate of 1% solids by weight on
15 cement. Samples are also stored at 20°C, 30°C and 40°C for six months. At the end of the six months, the admixtures remained visually unaffected. The actual test results are shown in the following table:

Sample No.		1	2	3	4
Storage time	[days]	1	180	180	180
Storage temperature	[°C]	20	20	30	40
W/C		0.42	0.42	0.42	0.42
Flow table	[cm]	16.5	18.0	17.0	18.0
Initial setting	[min.]	500	450	400	330
Final setting	[min.]	920	850	740	740

- 20 It can be seen that the properties are only slightly changed.

CLAIMS:

1. A fluidising admixture for use with sprayable cementitious compositions, the admixture consisting of

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(1) 2-phosphonobutane-1,2,4-tricarboxylic acid;

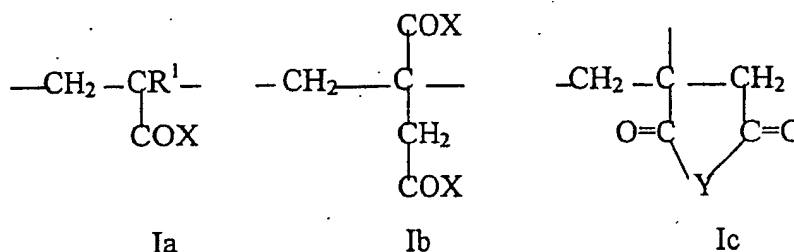
(2) optionally, citric acid; and

10

(3) at least one polymer derived from ethylenically-unsaturated mono- or dicarboxylic acids, and characterised in that the polymer consists of

a) 51-95 mole % of moieties of formula 1a and/or 1b and/or 1c

15



20

wherein R^1 = hydrogen or a C_{1-20} aliphatic hydrocarbon residue;

$X = O_a M$, $-O-(C_m H_{2m} O)_n - R^2$, $-NH-(C_m H_{2m} O)_n - R^2$,

M = hydrogen, a mono- or divalent metal cation, an ammonium ion or an organic amine residue;

25

$a = 0.5$ or 1 ;

R^2 = hydrogen, C_{1-20} aliphatic hydrocarbon, C_{5-8} cycloaliphatic hydrocarbon or optionally substituted C_{6-14} aryl residue;

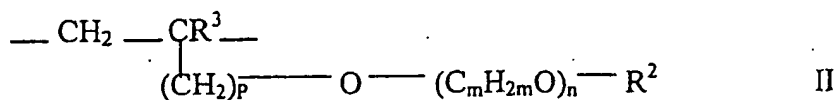
$Y = O$, NR^2 ;

$m = 2-4$; and

30

$n = 0-200$

b) 1-48.9 mole% of moieties of the general formula II

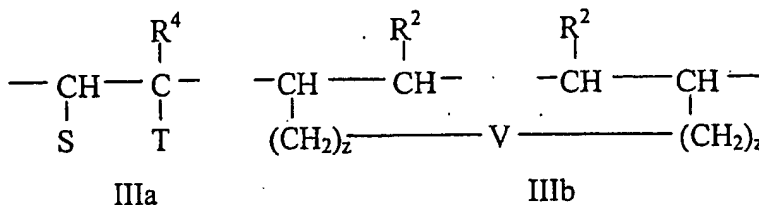


wherein R^3 = hydrogen or C_{1-5} aliphatic hydrocarbon;

$p = 0-3$; and

R^2 has the meaning given previously;

c) 0.1-5 mole % of moieties of Formulae IIIa or IIIb



wherein $\text{S} = \text{H}, -\text{COO}_a\text{M}, -\text{COOR}^5$

$\text{T} = \text{U}^1\text{---}(\underset{\substack{| \\ \text{CH}^3}}{\text{CH}}\text{---CH}_2\text{---O})_x\text{---}(\text{CH}_2\text{---CH}_2\text{O})_y\text{---R}^6$

$-\text{W-R}^7$

$-\text{CO-[NH-(CH}_2)_3]_s\text{---W-R}^7$

$-\text{CO-O-(CH}_2)_z\text{---W-R}^7$

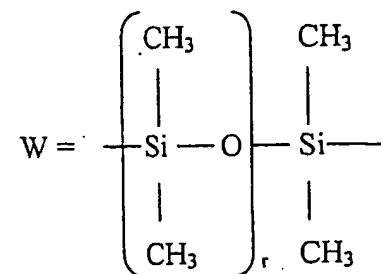
$-(\text{CH}_2)_z\text{---V-(CH}_2)_z\text{---CH=CH-R}^2$

$= -\text{COOR}^5$ when S is $-\text{COOR}^5$ or COO_aM

$\text{U}^1 = -\text{CO-NH-}, -\text{O-}, -\text{CH}_2\text{O-}$

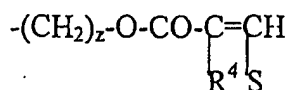
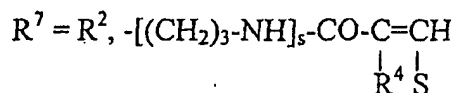
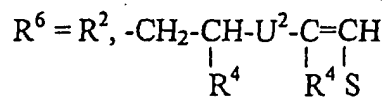
$\text{U}^2 = -\text{NH-CO-}, -\text{O-}, -\text{OCH}_2\text{-}$

$\text{V} = -\text{O-CO-C}_6\text{H}_4\text{-CO-O-}$ or $-\text{W-}$



$\text{R}^4 = \text{H}, \text{CH}_3$

R^5 = a C_{3-20} aliphatic hydrocarbon residue, a C_5-C_8 cycloaliphatic hydrocarbon residue or a C_6-14 aryl residue;



wherein

$$r = 2-100$$

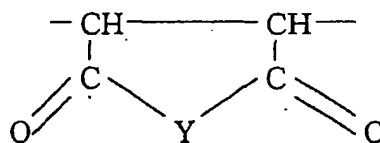
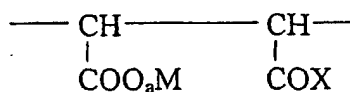
$$s = 1, 2$$

$$z = 0-4$$

$$x = 1-150$$

$$y = 0-15$$

d) 0-47.9 mole % of moieties of the general formula IVa and / or IV b:



IVa

IVb

wherein a, M, X and Y have the significances hereinabove defined.

2. A fluidising admixture according to claim 1, in which

a) the moiety is according to formula Ia;

R^1, R^2 are independently H or CH_3 ;

$X = O_a M, -O-(C_m H_{2m} O)_n - R^2$

$M = H$ or a mono-or divalent metal cation;

$a = 1$;

$Y = O, NR^2$;

m= 2-3; and

n= 20-150;

b) R^2, R^3 are independently H or CH_3 ; and

p = 0-1;

c) the moiety is according to formula IIIa;

$S = H, -COO_aM, -COOR^5$

$T = U^1 - \underset{\text{CH}^3}{\underset{|}{(CH-CH_2-O)}_x} - (CH_2-CH_2O)_y R^6$

$-CO-[NH-(CH_2)_3]_s-W-R^7$

$-CO-O-(CH_2)_z-W-R^7$

R^4, R^5 are independently H, CH_3 ;

$R^6 = R^2, -CH_2-\underset{\text{R}^4}{\underset{|}{CH}}-U^2-\underset{\text{R}^4}{\underset{|}{C}}=\underset{\text{S}}{\underset{|}{CH}}$

$R^7 = R^2, -[(CH_2)_3-NH]_5-CO-\underset{\text{R}^4}{\underset{|}{C}}=\underset{\text{S}}{\underset{|}{CH}}$

$-(CH_2)_z-O-CO-\underset{\text{R}^4}{\underset{|}{C}}=\underset{\text{S}}{\underset{|}{CH}}$

wherein

$U^1 = -CO-NH-, -O-, -CH_2O-$

$U^2 = -NH-CO-, -O-, -OCH_2-$

x = 20-50;

y = 1-10; and

z = 0-2.

3. A fluidising admixture according to claim 2, in which

a) the moiety is according to formula Ia;

$R^1 = H$;

$R^2 = CH_3$;

$X = O_a M$;

M = a mono-or divalent metal cation;

$Y = O, NR^2$;

$m = 2$; and

$n = 25-50$;

5 b) $R^2, R^3 = H$; and

$p = 0$;

c) the moiety is according to formula IIIa;

$S = H, -COO_aM$;

10 $T = U^1 - (\underset{\text{CH}^3}{\text{CH}} - \text{CH}_2 - \text{O})_x - (\text{CH}_2 - \text{CH}_2\text{O})_y R^6$

$-\text{CO}-\text{O}-(\text{CH}_2)_z-\text{W}-R^7$

$R^4, R^5 = H$;

15 $R^6 = R^2, -\text{CH}_2-\underset{\text{R}^4}{\text{CH}}-\text{U}^2-\underset{\text{R}^4}{\text{C}}=\underset{\text{S}}{\text{CH}}$

$R^7 = R^2, -[(\text{CH}_2)_3-\text{NH}]_5-\text{CO}-\underset{\text{R}^4}{\text{C}}=\underset{\text{S}}{\text{CH}}$

20 $-(\text{CH}_2)_z-\text{O}-\text{CO}-\underset{\text{R}^4}{\text{C}}=\underset{\text{S}}{\text{CH}}$

wherein

$U^1 = -\text{CO}-\text{NH}-$;

$U^2 = -\text{NH}-\text{CO}-, -\text{O}-, -\text{OCH}_2-$

$x = 20-50$;

25 $y = 5-10$; and

$z = 1-2$.

4. A method of imparting flow to a cementitious composition, comprising the addition thereto of an admixture according to any one of claims 1-3.

30

5. A method of spraying a cementitious composition by preparing a cementitious mix and conveying the mix to a spray nozzle, there being added to the mix at preparation an admixture according to claim 1.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 02/10045

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C04B24/00 C04B24/06 C04B24/26		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C04B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 508 158 A (SIKA AG) 14 October 1992 (1992-10-14) the whole document	1-5
Y	GB 2 347 415 A (MBT HOLDING AG) 6 September 2000 (2000-09-06) page 1, line 30 -page 8, line 5	1-4
Y	WO 00 77058 A (LEITNER HUBERT ;HUEBSCH CHRISTIAN (DE); GRASSL HARALD (DE); KERN A) 21 December 2000 (2000-12-21) cited in the application page 4, line 13 -page 22, line 18	1-5
A	CH 678 526 A (SANDOZ AG) 30 September 1991 (1991-09-30) column 1, line 61 -column 3, line 63	
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*g* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">12 March 2003</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">28/03/2003</div>
Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo.nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Gattinger, I</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

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